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Scaling analysis of the viscoelastic response of linear polymers

Mohamed F., Flämig M., Hofmann M., Heymann L., Willner L., Fatkullin N., Aksel N., Rössler E.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2018 Author(s). Viscoelastic response in terms of the complex shear modulus G∗(ω) of the linear polymers poly(ethylene-alt-propylene), poly(isoprene), and poly(butadiene) is studied for molar masses (M) from 3k up to 1000k and over a wide temperature range starting from the glass transition temperature Tg(174 K-373 K). Master curves G′(ωτα) and G″(ωτα) are constructed for the polymer-specific relaxation. Segmental relaxation occurring close to Tgis independently addressed by single spectra. Altogether, viscoelastic response is effectively studied over 14 decades in frequency. The structural relaxation time ταused for scaling is taken from dielectric spectra. We suggest a derivative method for identifying the different power-law regimes and their exponents along G″(ωτα) â ωϵ″. The exponent ϵ″ = ϵ″(ωτα) â‰¡ d ln G″(ωτα)/d ln(ωτα) reveals more details compared to conventional analyses and displays high similarity among the polymers. Within a simple scaling model, the original tube-reptation model is extended to include contour length fluctuations (CLFs). The model reproduces all signatures of the quantitative theory by Likhtman and McLeish. The characteristic times and power-law exponents are rediscovered in ϵ″(ωτα). The high-frequency flank of the terminal relaxation closely follows the prediction for CLF (ϵ″ = -0.25), i.e., G″(ω) â ω-0.21±0.02. At lower frequencies, a second regime with lower exponent ϵ″ is observed signaling the crossover to coherent reptation. Application of the full Likhtman-McLeish calculation provides a quantitative interpolation of ϵ″(ωτα) at frequencies below those of the Rouse regime. The derivative method also allows identifying the entanglement time τe. However, as the exponent in the Rouse regime (ωτe> 1) varies along ϵeRouse= 0.66 ± 0.04 (off the Rouse prediction ϵRouse= 0.5) and that at ωτe< 1 is similar, only a weak manifestation of the crossover at τeis found at highest M. Yet, calculating τe/τα= (M/Mo)2, we find good agreement among the polymers when discussing ϵ″(ωτe). The terminal relaxation time τtis directly read off from ϵ″(ωτα). Plotting τt/τeas a function of Z = M/Me, we find universal behavior as predicted by the TR model. The M dependence crosses over from an exponent significantly larger than 3.0 at intermediate M to an exponent approaching 3.0 at highest M in agreement with previous reports. The frequency of the minimum in G″(ωτα) scales as τmin∞ M1.0±0.1. An M-independent frequency marks the crossover to glassy relaxation at the highest frequencies. Independent of the amplitude of G″(ω), which may be related to sample-to-sample differences, the derivative method is a versatile tool to provide a detailed phenomenological analysis of the viscoelastic response of complex liquids.

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References

[1] P. G. deGennes, "Reptation of a polymer chain in the presence of fixed obstacles," J. Chem. Phys. 55, 572 (1971). 10.1063/1.1675789

[2] M. Doi and S. F. Edwards, The Theory of Polymer Dynamics (Oxford Scientific Publication, 1986).

[3] A. E. Likhtman and T. C. B. McLeish, "Quantitative theory for linear dynamics of linear entangled polymers," Macromolecules 35, 6332 (2002). 10.1021/ma0200219

[4] M. Abdel-Goad, W. Pyckhout-Hintzen, S. Kahle, J. Allgaier, D. Richter, and L. J. Fetters, "Rheological proterties of 1,4-polybutadienen over a large molecular weight range," Macromolecules 37, 8135 (2004). 10.1021/ma030557+

[5] D. Auhl, J. Ramirez, A. E. Likhtman, P. Chambon, and Ch. Fernyhough, "Linear and nonlinear shear flow behavior of monodisperse polyisoprene melts with a large range of molecular weights," J. Rheol. 52, 801 (2008). 10.1122/1.2890780

[6] A. Wischnewski, M. Monkenbusch, L. Willner, D. Richter, and G. Kali, "Direct observation of the transition from free to constrained single-segment motion in entangled polymer melts," Phys. Rev. Lett. 90, 058302 (2003). 10.1103/physrevlett.90.058302

[7] D. Richter, M. Monkenbusch, A. Arbe, and J. Colmenero, "Neutron spin echo in polymer systems," Adv. Polym. Sci. 174, 1 (2005). 10.1007/b99835

[8] M. Kehr, N. Fatkullin, and R. Kimmich, "Molecular diffusion on a time scale between nano- and milliseconds probed by field-cycling NMR relaxometry of intermolecular dipolar interaction: Applications to polymer melts," J. Chem. Phys. 126, 094903 (2007). 10.1063/1.2435357

[9] A. Herrmann, B. Kresse, M. Wohlfart, I. Bauer, A. F. Privalov, D. Kruk, N. Fatkullin, F. Fujara, and E. A. Rössler, "Mean square displacement and reorientational correlation function in entangled polymer melts revealed by field cycling H and H NMR relaxometry," Macromolecules 45, 6516 (2012). 10.1021/ma301099h

[10] B. Kresse, M. Hofmann, A. F. Privalov, F. Fujara, N. Fatkullin, and E. A. Rössler, "All polymer diffusion regimes covered by combining field-cycling and field-gradient H NMR," Macromolecules 48, 4491 (2015). 10.1021/acs.macromol.5b00855

[11] M. Hofmann, B. Kresse, A. F. Privalov, L. Heymann, L. Willner, N. Aksel, N. Fatkullin, F. Fujara, and E. A. Rössler, "Segmental mean square displacement: Field-cycling H relaxometry vs. neutron scattering," Macromolecules 49, 7945 (2016). 10.1021/acs.macromol.6b01860

[12] M. Doi, "Explanation for the 3,4-power law for viscosity of polymeric liquids on the basis of the tube model," J. Polym. Sci.: Phys. Ed. 21, 667 (1983). 10.1002/pol.1983.180210501

[13] M. Rubinstein and R. H. Colby, "Self-consistent theory of polydisperse entangled polymers: Linear viscoelasticity of binary blends," J. Chem. Phys. 89, 5291 (1988). 10.1063/1.455620

[14] J. D. Cloizeaux, "Relaxation and viscosity anomaly of melts made of long entangled polymers: Time-dependent reptation," Macromolecules 23, 4678 (1990). 10.1021/ma00223a028

[15] C.-Y. Liu, R. Keunings, and C. Bailly, "Direct rheological evidence of monomer density reequilibration for entangled polymer melts," Macromolecules 40, 2946 (2007). 10.1021/ma062695f

[16] S. J. Park, P. S. Desai, X. Chen, and R. G. Larson, "Universal relaxation behavior of entangled 1,4-polybutadiene melts in the transition frequency region;" Macromolecules 48, 4122 (2015). 10.1021/ma5024632

[17] L. Szanto, R. Vogt, J. Meier, D. Auhl, E. Van Ruymbeke, and C. Friedrich, "Entanglement relaxation time of polyethylene melts from high-frequency rheometry in the mega-hertz range," J. Rheol. 61, 1023 (2017). 10.1122/1.4998174

[18] M. Hofmann, N. Fatkullin, and E. A. Rössler, "Inconsistencies in determining the entanglement time of poly(butadiene) from rheology and comparison to results from field-cycling NMR," Macromolecules 50, 1755 (2017). 10.1021/acs.macromol.6b02546

[19] D. Ferry, Viscoelastic Properties of Polymers (John Wiley & Sons, New York 1980).

[20] R. H. Colby, L. J. Fetters, and W. W. Graessley, "Melt viscosity-molecular weight relationship for linear polymers," Macromolecules 20, 2226 (1987). 10.1021/ma00175a030

[21] M. Rubinstein and R. H. Colby, Polymer Physics (Oxford University Press, Oxford, UK, 2003).

[22] W. W. Graessley, Polymeric Liquids and Networks: Dynamics and Rheology, Polymeric Liquids and Networks: Structure and Properties (Taylor and Francis, New York, 2008).

[23] M. Hofmann, B. Kresse, L. Heymann, A. F. Privalov, N. Fatkullin, N. Aksel, F. Fujara, and E. A. Rössler, "Dynamics of a paradigmatic linear polymer: A proton field-cycling NMR relaxometry study on poly(ethylene-propylene)," Macromolecules 49, 8622 (2016). 10.1021/acs.macromol.6b01906

[24] S. Kariyo, A. Brodin, C. Gainaru, A. Herrmann, H. Schick, V. N. Novikov, and E. A. Rössler, "From simple liquid to polymer melt. Glassy and polymer dynamics studied by field cycling NMR relaxometry: Low and high molecular weight limit," Macromolecules 41, 5313 (2009). 10.1021/ma702771s

[25] A. A. Elfadl, A. Herrmann, V. N. Novikov, and E. A. Rössler, "From Rouse to entanglement dynamics-A study of polyisoprene by dielectric spectroscopy," Macromolecules 43, 3340 (2010). 10.1021/ma902564b

[26] B. Schmidtke, M. Hofmann, A. Lichtinger, and E. A. Rössler, "Temperature dependence of the segmental relaxation time of polymers revisited," Macromolecules 48, 3005 (2015). 10.1021/acs.macromol.5b00204

[27] T. Körber, F. Mohamed, M. Hofmann, A. Lichtinger, L. Willner, and E. A. Rössler, "On the nature of secondary relaxations: The case of poly(ethylene-alt-propylene) studied by dielectric and deuteron NMR spectroscopy," Macromolecules 50, 1554 (2017). 10.1021/acs.macromol.6b02536

[28] C. B. Gell, W. W. Graessley, and L. J. Fetters, "Viscoelasticity and self-diffusion in melts of entangled linear polymers," J. Polym. Sci. Part B: Polym. Phys. 35, 1933 (1997). 10.1002/(sici)1099-0488(19970915)35:12<1933::aid-polb8>3.0.co;2-q

[29] K. Nusser, G. J. Schneider, and D. Richter, "Rheology and anomalous flow properties of poly(ethylene-al--propylene)-silica nanocomposites," Macromolecules 46, 6263 (2013). 10.1021/ma3025927

[30] T. Glomann, G. Schneider, R. Bras, W. Pyckhout-Hintzen, A. Wischnewski, R. Zorn, J. Allgaier, and D. Richter, "Unified description of the viscosity and the dielectric global chain motion in terms of the tube theory," Macromolecules 44, 7430 (2011). 10.1021/ma200674z

[31] D. J. Plazek and V. M. O'Rourke, "Viscoelastic Behavior of low molecular weight polystyrene," J. Polym. Sci., Part A-2 9, 209 (1971). 10.1002/pol.1971.160090202

[32] D. J. Plazek, X. D. Zheng, and K. L. Ngai, "Viscoelastic properties of amorphous polymers. I. Different temperature dependences of segmental relaxation and terminal dispersion," Macromolecules 25, 4920 (1992). 10.1021/ma00045a016

[33] T. Inoue, H. Okamoto, and K. Osaki, "Birefringence of amorphous polymers. 1. Dynamic measurement on polystyrene," Macromolecules 24, 5670 (1991). 10.1021/ma00020a029

[34] Y. Ding and A. P. Sokolov, "Breakdown of timeerature superposition principle and universality of chain dynamics in polymers," Macromolecules 39, 3322 (2006). 10.1021/ma052607b

[35] L. I. Pallade, V. Verney, and P. Attane, "Timeerature superposition and linear viscoelasticity of polybutadienes," Macromolecules 28, 7051 (1995). 10.1021/ma00125a003

[36] A. Benallal, G. Marin, J. P. Monfort, and C. Derail, "Linear viscoelasticity revisited: The relaxation function of monodisperse polymer melts," Macromolecules 26, 7229 (1993). 10.1021/ma00078a018

[37] A. Herrmann, B. Kresse, J. Gmeiner, A. F. Privalov, D. Kruk, F. Fujara, and E. A. Rössler, "Protracted crossover to reptation dynamics: A field cycling H NMR study including extremely low frequencies," Macromolecules 45, 1408 (2012). 10.1021/ma202489y

[38] K. Nusser, S. Neueder, G. J. Schneider, M. Meyer, W. Pyckhout-Hintzen, L. Willner, A. Radulescu, and D. Richter "Conformations of silica-poly(ethylene-propylene) nanocomposites "Macromolecules 43, 9837 (2010). 10.1021/ma101898c

[39] Ch. Ohrt, T. Koschine, K. Rätzke, F. Faupel, L. Willner, and G. J. Schneider, "Free-volume in PEP-silica nanocomposites with varying molecular weight," Polymer 55, 143 (2014). 10.1016/j.polymer.2013.11.021

[40] K. Schröter, S. A. Hutcheson, X. Shi, A. Mandanici, and G. B. McKenna, "Dynamic shear modulus of glycerol: Corrections due to instrument compliance," J. Chem. Phys. 125, 214507 (2006). 10.1063/1.2400862

[41] J. Läuger and H. Stettin, "Radial compliance in oscillatory measurements," Technical note, Anton Paar Germany GmbH, 2010.

[42] T. Nill, "Measurement of glycerol in the glassy state-investigation and correction of instrument radial compliance," Extended Application Report, Anton Paar Germany GmbH, 2014.

[43] K. Schröter and E. Donth, "Viscosity and shear response at the dynamic glass transition of glycerol," J. Chem. Phys. 113, 9101 (2000). 10.1063/1.1319616

[44] M. Hofmann, C. Gainaru, B. Cetinkaya, R. Valiullin, N. Fatkullin, and E. A. Rössler, "Field-cycling relaxometry as a molecular rheology technique: Common analysis of NMR, shear modulus and dielectric loss data of polymers vs. dendrimers," Macromolecules 48, 7521 (2015). 10.1021/acs.macromol.5b01805

[45] R. Kahlau, D. Kruk, T. Blochowicz, V. N. Novokov, and E. A. Rössler, "Generalizationof the Cole-Davidson and Kohlrausch functions to describe the primary response of glass-forming systems," J. Phys.: Condens. Matter 22, 365101 (2010). 10.1088/0953-8984/22/36/365101

[46] W. Götze and L. Sjögren, "Relaxation processes in supercooled liquids," Rep. Prog. Phys. 55, 241 (1992). 10.1088/0034-4885/55/3/001

[47] H. J. Unidad, M. A. Goad, A. R. Bras, M. Zamponi, R. Faust, J. Allgaier, W. Pyckhout-Hintzen, A. Wischnewski, D. Richter, and L. J. Fetters, "Consequences of increasing packing length on the dynamics of polymer melts," Macromolecules 48, 6638 (2015). 10.1021/acs.macromol.5b00341

[48] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, and A. Zirkel, "Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties," Macromolecules 27, 4639 (1994). 10.1021/ma00095a001

[49] J. Ramirez and A. E. Likhtman, "Rheology of entangled polymers: Toolkit for analysis of theory & experiment," http://www.reptate.com/, Version 1.0, 14 April 2009.

[50] M. Baumgaertel, A. Schausberger, and H. H. Winter, "The relaxation of polymers with flexible chain of uniform length," Rheol. Acta 29, 400 (1990). 10.1007/bf01376790

[51] E. W. Montroll and J. T. Bendler, "On Levy (or stable) distributions and the Williams-Watts model of dielectric relaxation," J. Stat. Phys. 34, 129 (1984). 10.1007/bf01770352